EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF LOW/MEDIUM CONCENTRATIONS
OF VOLATILE ORGANIC COMPOUNDS

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of volatiles in hazardous waste samples. These methods were based on USEPA Method 624, Purgeables. In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis for other USEPA methods to perform the analysis of volatiles contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of volatiles at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites for the volatile organic compounds on the Target Compound List (TCL) in Exhibit C (Low/Medium Volatiles). The method includes sample preparation and analysis to determine the approximate concentration of organic constituents in the sample. The actual analysis is based on a purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) method for aqueous and medium-level soil samples and closed-system purge-and-trap for low-level soil samples.

1.3 Problems have been associated with the following compounds analyzed by this method.

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.

- Acetone, hexanone, 2-butanone, 4-methyl-2-pentanone, and 1,4-dioxane have poor purge efficiencies.

- 1,1,1-trichloroethane and all the dichloroethanes can dehydrohalogenate during storage or analysis.

- Chloromethane may be lost if the purge flow is too fast.

- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by tuning of 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio within the specified Quality Control (QC) limits may improve bromoform response.

2.0 SUMMARY OF METHOD

2.1 Water

An inert gas is bubbled through a 5 mL sample contained in a specifically designed purging chamber at ambient temperature. Higher purge temperatures may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks. The same purge conditions must be used for all associated standards, samples, and blanks. The purgeable compounds are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a Gas Chromatographic (GC) column. The GC is temperature-programmed to separate the purgeable compounds which are then detected with a Mass Spectrometer (MS).

2.2 Low-Level Soil/Sediment

Low-level volatile organic compounds are generally determined by analyzing approximately 5 g of sample, in a pre-weighed vial with a septum-sealed screw-cap (see Section 6.0) that already contains a stirring bar.

NOTE: The sodium bisulfate preservative may be used under limited circumstances. 5.0 mL of sodium bisulfate solution (Section 7.1.3) is added to each sample when preservation by sodium bisulfate is requested by the Region.

The entire vial is placed into the instrument carousel. Immediately before analysis, organic-free reagent water, Deuterated Monitoring Compounds (DMCs), and internal standards are automatically added without opening the sample vial. The vial containing the sample is heated to the suggested temperature of 40°C and the volatiles are purged through a sorbent trap using an inert gas combined with agitation of the sample. Higher purge temperatures may be required for the analysis of certain target compounds (i.e., 1,4-dioxane). When purging is complete, the trap is heated and backflushed with helium to desorb the purgeable compounds onto a GC column. The GC is temperature-programmed to separate the purgeable compounds which are then detected with an MS.

2.3 Medium-Level Soil/Sediment

A soil sample of 5 g is collected, preserved in methanol and/or extracted with methanol. An aliquot of the methanol extract is added to 5 mL of reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The purgeable compounds are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a GC column. The GC is temperature-programmed to separate the purgeable compounds which are then detected with an MS.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 12. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples must be stored separately from other laboratory samples and standards, and must be analyzed in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine the presence of methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken. At the time of sample receipt, the Contractor must prepare two 40 mL VOA vials containing reagent water and/or inert sand to be stored with each group of samples (Section 12.1.1.2).

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analyses.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene; carbon tetrachloride; chloroform; vinyl chloride; and 1,4-dioxane. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Sample Containers

The specific required sample containers will depend on the purge-and-trap system to be employed. Several systems are commercially available. Some systems employ 40 mL clear vials with a special frit and equipped with two polytetrafluoroethylene (PTFE)-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water, and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. The Contractor shall consult the purge-and-trap system manufacturer’s instructions regarding suitable specific vials, septa, caps, and mechanical agitation devices.

6.2 Glassware

6.2.1 Syringes - 25 mL glass hypodermic syringes with a Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used). 5.0, 1.0, and 0.5 mL syringes, gas-tight with shut-off valve.

6.2.2 Syringe Valve - Two-way, with Luer ends (three each), if applicable to the purging device.

6.2.3 Micro Syringes - 25 µL with a 2 inch x 0.006 inch ID, 22 gauge beveled needle. 10 µL, 100 µL.

6.2.4 Disposable Pasteur Pipets.

6.2.5 Volumetric Flasks - Class A, 10 mL and 100 mL, with ground glass stoppers.

6.2.6 60 mL, septum-sealed glass vials to collect samples for screening, percent moisture determination.

6.2.7 40 mL, screw-cap, PTFE-lined, septum-sealed glass vials. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

6.2.8 Vials and Caps - Assorted sizes.

6.2.9 Bottle - 15 mL, screw-cap, with PTFE capliner.

6.3 pH Paper - Wide range

6.4 Magnetic Stirring Bars

PTFE or glass-coated, of the appropriate size to fit the sample vials. Consult the manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturer of the purging device and the stirring bars for suggested cleaning procedures.

6.5 Balances

Balances must be analytical and capable of accurately weighing ±0.0001 g. The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with Class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

6.6 Purge-and-Trap Device

The purge-and-trap device consists of three separate pieces of equipment: the sample purge chamber, the trap, and the desorber. This device either manually or automatically: samples an appropriate volume (e.g., 5.0 mL from the vial), adds DMCs, matrix spikes and internal standards to the sample and transfers the sample to the purge device. This device also purges the volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the gas chromatograph. For low-level soil samples, the purge-and-trap device consists of: a unit that automatically adds water, DMCs, and internal standards to a hermetically sealed vial containing the sample; purges the volatile compounds using an inert gas stream while agitating the contents of the vial; and traps the released volatile compounds for subsequent desorption into the Gas Chromatograph (GC). Such systems are commercially available from several sources and shall meet the following specifications.

6.6.1 The sample purge chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.6.2 For soil samples, the purging device should be capable of accepting a vial large enough to contain a 5 g soil/sediment sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the

displaced headspace vapors. It must also be capable of agitating the sealed sample during purging (e.g., using a magnetic stirring bar, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed volatile compounds to the GC.

6.6.3 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches (2.667 mm). The trap must be packed to contain (starting from the inlet) 0.5 cm silanized glass wool, and the following minimum lengths of absorbent:

- 8 cm of 2,6-diphenylene oxide polymer (60/80 mesh chromatographic grade Tenax GC or equivalent).
- 1 cm methyl silicone packing, 3.0% OV-1 on Chromasorb W, 60/80 mesh (or equivalent).
- 8 cm of silica gel, 35/60 mesh (or equivalent).
- 7 cm of coconut charcoal.

6.6.4 Alternate sorbent traps may be used if:

- The trap packing materials do not introduce contaminants that interfere with identification and quantitation of the compounds listed in Exhibit C (Low/Medium Volatiles).
- The analytical results generated using the trap meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Low/Medium Volatiles).
- The trap can accept up to 1000 ng of each compound listed in Exhibit C (Low/Medium Volatiles) without becoming overloaded.

6.6.4.1 The alternate trap must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any trap, other than the one specified in Section 6.6.3, the Contractor must first meet the criteria listed in Section 6.6.4. Once this has been demonstrated, the Contractor must document its use in each SDG Narrative by specifying the trap composition (packing material/brand name, amount of packing material). Other sorbent traps include, but are not limited to, Tenax/Silica Gel/Carbon Trap from USEPA Method 524.2, Tenax - GC/Graphpac-D Trap (Alltech) or equivalent, and Vocarb 4000 Trap (Supelco) or equivalent.

6.6.4.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.6.4. The minimum documentation requirements are as follows:

6.6.4.2.1 Manufacturer provided information concerning the performance characteristics of the trap.

6.6.4.2.2 Reconstructed ion chromatograms and data system reports generated on the Contractor's Gas Chromatograph/Mass Spectrometer (GC/MS) used for Contract Laboratory Program (CLP) analyses:

- From instrument blank analyses that demonstrate there are no contaminants that interfere with the volatile analysis when using the alternate trap;

- From initial and continuing calibration verification standards analyzed using the trap specified in Section 6.6.3.

6.6.4.2.3 Based on Contractor-generated data described above, the Contractor must complete a written comparison/review, that has been signed by the Laboratory Manager certifying that:

- The alternate trap performance meets the technical acceptance criteria listed in Sections 9.3.5 and 9.4.5;

- The low-point initial calibration standard analysis has adequate sensitivity to meet the low/medium volatile CRQLs;

- The high-point initial calibration standard analysis was not overloaded; and

- The alternate trap materials do not introduce contaminants that interfere with the identification and/or quantitation of the compounds listed in Exhibit C (Low/Medium Volatiles).

6.6.4.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA Regional CLP Project Officer (CLP PO).

6.6.5 The purge-and-trap apparatus may be assembled as a separate unit or be an integral unit coupled with a GC.

6.6.6 The desorber should be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bake-out mode.

6.7 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.7.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a purge-and-trap system as specified in Section 6.6 and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants, or flow controllers with rubber components are not to be used.

6.7.2 GC Columns - A description of the column used for analysis shall be provided in the SDG Narrative.

6.7.2.1 Minimum length 30 m x 0.53 mm ID VOCOL, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.2 Minimum length 30 m x 0.53 mm ID DB-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.3 Minimum length 30 m x 0.53 mm ID AT-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.4 Minimum length 30 m x 0.53 mm ID Rtx-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.5 Minimum length 30 m x 0.53 mm ID BP-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.6 Minimum length 30 m x 0.53 mm ID CP-Select 624CB, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.3 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Low/Medium Volatiles).
- The analytical results generated using the column meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method, and the CRQLs listed in Exhibit C (Low/Medium Volatiles).
- The column provides equal or better resolution of the compounds listed in Exhibit C (Low/Medium Volatiles) than the columns listed in Section 6.7.2.

6.7.3.1 As applicable, follow the manufacturer's instructions for use of its product.

6.7.3.2 The Contractor must maintain documentation that the column met the criteria in Section 6.7.3. The minimum documentation is as follows:

6.7.3.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.7.3.2.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for the CLP analyses:

- From instrument blanks that demonstrate that there are no contaminants that interfere with the volatile analysis when using the alternate column; and
- From initial and continuing calibration verification standards analyzed using the alternate column.

6.7.3.2.3 Based on the Contractor-generated data described above, the Contractor shall complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the low/medium volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The column does not introduce contaminants that interfere with the identification and/or quantitation of compounds listed in Exhibit C (Low/Medium Volatiles).

6.7.3.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request by the USEPA Regional CLP PO.

6.7.4 **PACKED COLUMNS CANNOT BE USED.**

6.7.5 Mass Spectrometer

Must be capable of scanning from 35 to 300 atomic mass unit (amu) every 2 seconds or less utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum that meets all the 4-bromofluorobenzene (BFB) GC/MS performance check technical acceptance criteria in Table 1 when 20 ng of BFB are injected through the GC inlet. The instrument conditions required for the acquisition of the BFB mass spectrum are given in Section 9.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge-and-trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.7.6 GC/MS Interface

Any GC/MS interface that gives acceptable calibration points at 25 ng or less, per injection for each of the parameters of interest, and achieves all acceptance criteria, may be used. GC to MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.7.7 Data System

A computer system interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST (2002 release or later) or equivalent mass spectral library shall be used as the reference library. The operational data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

6.7.8 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a polytetrafluoroethylene (PTFE)-lined septum and cap.

7.1.2 Methanol - Pesticide quality or equivalent.

7.1.3 Sodium Bisulfate Solution - 2.0 g of ACS reagent grade or equivalent sodium bisulfate is dissolved for every 5.0 g of water.

7.2 Standards

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer’s expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions, prepared by the Contractor which are immediately ampulated in glass vials, may be retained for 2 years from the preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.1 - 7.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (see Section 7.3.5).

7.2.1 Stock Standard Solutions

Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be prepared in methanol from pure standard materials, or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Instrument Performance Check Solution

Prepare the instrument performance check solution containing 4-bromofluorobenzene (BFB). If the BFB solution is added to the mid-level calibration standard (50 µg/L for non-ketones and 100 µg/L for ketones) add a sufficient amount of BFB to result in a 10 µg/L concentration of BFB (50 ng on column).

7.2.2.2 Calibration Standard Solution

Prepare the working calibration standard solution containing all of the purgeable target compounds in methanol [Exhibit C (Low/Medium Volatiles)]. Prepare a fresh calibration standard solution monthly, or sooner if the solution has degraded or evaporated. The recommended concentration of the target compounds is 100 µg/mL.

NOTE: The Contractor may prepare a calibration standard containing all of the non-ketones and a separate standard containing the ketones.

7.2.2.3 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 in methanol. Add a sufficient amount of the internal standard solution to 5 mL of samples, including Matrix Spike and Matrix Spike Duplicates (MS/MSD), blanks, and calibration standards to result in a 50.0 µg/L concentration. Prepare a fresh internal standard solution weekly, or sooner if the solution has degraded or evaporated.

7.2.2.4 Deuterated Monitoring Compound (DMC) Spiking Solution

Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed below: DMCs are to be added to each sample and blank, as well as initial calibration standards and continuing calibration verification standards. For samples and blanks, add sufficient amount of DMC solution to each 5 mL of sample to result in a concentration of 50 µg/L of each non-ketone DMC, 100 µg/L for each ketone DMC, and 1250 µg/L for 1,4-dioxane-d_8 DMC. For calibration standards, add sufficient amounts of DMC solution to each 5 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.6.2 (initial calibration) and Section 7.2.2.6.4 (continuing calibration verification). Prepare a fresh DMC solution every month, or sooner if the standard has degraded.

Compound

Vinyl chloride-d_3

Chloroethane-d_5

1,1-Dichloroethene-d_2

2-Butanone-d_5

Chloroform-d

1,2-Dichloroethane-d_4

Benzene-d_6

1,2-dichloropropane-d_6

Toluene-d_8

trans-1,3-Dichloropropene-d_4

2-Hexanone-d_5

1,4-Dioxane-d_8

1,1,2,2-Tetrachloroethane-d_2

1,2-Dichlorobenzene-d_4

7.2.2.5 Matrix Spiking Solution

If MS/MSD analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following compounds at a concentration of 12.5 µg/mL: 1,1-dichloroethene; trichloroethene; chlorobenzene; toluene; and benzene. Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.2.6 Initial and Continuing Calibration Verification Standards

7.2.2.6.1 Add a sufficient amount of each working standard to a 5 mL aliquot of reagent water to produce the desired calibration standard concentrations listed in Section 7.2.2.6.2 and 7.2.2.6.4.

7.2.2.6.2 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds and the DMCs at the following levels: all non-ketone target compounds and non-ketone DMCs at 5, 10, 50, 100, and 200 µg/L; all ketones and their associated DMCs at 10, 20, 100, 200, and 400 µg/L; 1,4-dioxane and 1,4-dioxane-d_8 DMC at 125, 250, 1250, 2500, and 5000 µg/L. All three xylene isomers (o-, m-, and p-xylene) must be present in the calibration standards. The o-xylene calibration standard concentrations must be at 5, 10, 50, 100, and 200 µg/L, while the concentration of the m-, plus p-xylene isomers must total 5, 10, 50, 100, and 200 µg/L.

7.2.2.6.3 Calibration standards may be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.2.6.4 The continuing calibration verification standard should be at or near the midpoint concentration level of the calibration standards, 50 µg/L for non-ketones, 100 µg/L for ketones and 1250 for 1,4-dioxane.

7.2.2.6.5 The methanol contained in each of the aqueous calibration standards must not exceed 1.0% by volume.

7.3 Storage of Standard Solutions

7.3.1 Store the stock standards in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C, and protect the standards from light.

7.3.2 Aqueous standards may be stored for up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at 4°C (±2°C). Protect the standards from light. If not stored as such, the standards must be discarded after 1 hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept up to 12 hours in purge tubes connected via the autosampler to the purge-and-trap device.

7.3.3 If standards are purchased and stored in ampulated vials, they may be stored up to 2 years after the preparation date.

7.3.4 Purgeable standards must be stored separately from other standards, samples, and blanks.

7.3.5 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

7.3.6 Temperature Records for Storage of Standards

7.3.6.1 The temperature of all standards storage refrigerators/freezers shall be recorded daily.

7.3.6.2 Temperature excursion shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.3.6.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Soil/Sediment Samples

8.1.1.1 Soil/Sediment samples may be received from the field either in pre-prepared closed-system purge-and-trap sample vials (Section 10.1.4), pre-weighed glass vials, or in field core sampling/storage containers (e.g., EnCore™ or equivalent). Samples received in pre-prepared closed-system vials may arrive with no added preservative, or preserved with sodium bisulfate. Samples in pre-weighed glass vials may be preserved with 10 mL of methanol (medium-level samples only). Only vials that are thoroughly sealed may be used for medium-level soil analysis.

8.1.1.2 For samples received in pre-prepared closed-system purge-and-trap vials or pre-weighed glass vials, the Contractor should receive at least two such vials per field sample, plus at least one additional 60 mL sealed glass vial containing sample with minimum headspace. For samples received in field core sampling containers, the Contractor should receive at least three such containers per field sample, plus at least one additional 60 mL sealed glass vial containing sample with minimum headspace. If the minimum amount of containers have not been sent by the field samplers, the Contractor is to immediately contact the Sample Management Office (SMO) for instructions. A total of 4 vials per field sample is the recommended amount of vials the Contractor should receive.

NOTE: If Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis is required for a particular sample, two additional field core containers or glass vials should be sent by the field samplers. Contact SMO if insufficient sample for MS/MSD analysis has been provided.

8.1.1.2.1 For each preserved sample, samplers should send approximately 5 g of sample unpreserved in a pre-weighed glass vial. The Contractor shall weigh this vial immediately upon receipt and then store at less than -7°C. If a medium-level analysis of the sample is necessary, use this vial.

8.1.1.3 Samples received in pre-prepared closed-system purge-and-trap vials without preservative are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C until time of analysis. Ensure that the samples are clean of external dirt and moisture prior to weighing.

8.1.1.4 In limited cases, preservation with sodium bisulfate may be required. Samples received in pre-prepared closed-system purge-and-trap vials preserved with sodium bisulfate shall be stored at 4°C (±2°C) until time of analysis. Samples preserved with bisulfate should be accompanied by field documentation recording the initial weight of the vial with preservative.

8.1.1.5 Medium-level samples may be received in pre-weighed vials preserved with methanol. If the volume of methanol in the vial does not appear to be equal to 10 mL, or if the vial appears to be dry, the Contractor shall immediately contact SMO, who will contact the Region. Samples preserved with methanol should be accompanied by field documentation recording the initial weight of the vial with methanol. Samples received preserved with methanol

shall be stored at 4°C (±2°C) until time of analysis. Samples received without preservative are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C until time of preparation and analysis.

8.1.1.6 For samples received in field core sampling/storage containers, the Contractor shall transfer the contents of two of the three containers for each sample, immediately upon receipt, to a pre-prepared closed-system purge-and-trap vial, and record the date and time of transfer. The transferred samples are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C.

8.1.2 Water Samples

8.1.2.1 Water samples should be collected in glass containers having a total volume of at least 40 mL with a polytetrafluoroethylene (PTFE)-lined septum and an open top screw-cap. Headspace should be avoided. The containers should be filled in such a manner that no air bubbles pass through the sample as the container is being filled. The samples are preserved to a pH of less than or equal to 2 at time of collection. Water samples shall be stored at 4°C (±2°C) until time of analysis. A total of 4 vials per field sample is the recommended amount the Contractor should receive.

8.2 Sample Storage

8.2.1 Unpreserved low/medium soil samples must be protected from light and stored at less than -7°C from the time of receipt until time of analysis. Store unused sample aliquots at less than -7°C until 60 days after delivery of a reconciled, complete Sample Data Package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Preserved low/medium soil samples and water samples must be protected from light and stored at 4°C (±2°C), in a refrigerator used only for storage of volatile samples, in an atmosphere demonstrated to be free of all potential contaminants, until 60 days after delivery of a reconciled, complete Sample Data Package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2.1 Aqueous storage blanks shall be stored with preserved low/medium soil samples and water samples within an SDG until all such samples are analyzed. Inert sand storage blanks shall be stored with unpreserved low/medium soil samples until all such samples are analyzed.

8.2.3 Samples, sample extracts, and standards must be stored separately. Volatile standards must be stored separately from semivolatile, pesticide, and Aroclor standards.

8.3 Temperature Records and Sample Storage

8.3.1 The temperature of all sample storage refrigerators and freezers shall be recorded daily.

8.3.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.3.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.4 Contract Required Holding Times

Analysis of water and soil/sediment samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples that the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The contract-required 10 day holding time does not apply to PE samples.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Purge-and-Trap

9.1.1.1 The following are the recommended purge-and-trap analytical conditions. The conditions are recommended unless otherwise noted.

Purge Conditions

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ±0.1 min.
Purge Flow Rate:	25-40 mL/min.
Purge Temperature:	Ambient temperature for water or medium-level soil/sediment samples (required for medium-level soil/sediment samples, suggested for water samples), and 40°C low-level soil/sediment samples (suggested). Higher purge temperatures may be used, provided that technical acceptance criteria are met for all standards, samples, and blanks. Certain target compounds, such as MTBE, may decompose at high purge temperatures in samples that have been acid preserved.

Desorb Conditions

Desorb Temperature:	180°C
Desorb Flow Rate:	15 mL/min. (4 mL/min. for low-level soil samples).
Desorb Time:	4.0 ±0.1 min.

Trap Reconditioning Conditions

Reconditioning Temperature:	180°C
Reconditioning Time:	7.0 ±0.1 min. (minimum). A longer time may be required to bake contamination or water from the system.

9.1.1.2 Assemble a purge-and-trap device that meets the specification in Section 6.6 and that is connected to a Gas Chromatograph/Mass Spectrometer (GC/MS) system.

9.1.1.3 Before initial use, condition the trap overnight at 180°C by backflushing with at least 20 mL/minute flow of inert gas according to the manufacturer’s recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, condition the trap for 10 minutes at 180°C while backflushing. The trap may be vented to the analytical column

during daily conditioning; however, the column must be run through the temperature program prior to the analysis of samples and blanks.

9.1.1.4 For low-level soil samples, establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of reagent water, to heat the sample to 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer. Once established, the same purge-and-trap conditions must be used for the analysis of all standards, samples, and blanks.

9.1.1.5 Optimize purge-and-trap conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same purge-and-trap conditions must be used for the analysis of all standards, samples, and blanks.

NOTE: In certain situations, a heated purge may be used for water samples provided that all standards, samples, and blanks are run under the same conditions and all technical acceptance criteria can be met.

9.1.1.6 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture or water if:

- The system does not introduce contaminants that interfere with identification and quantitation of compounds listed in Exhibit C (Low/Medium Volatiles);
- The analytical results generated when using the moisture reduction/water management system meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Low/Medium Volatiles);
- All calibration standards, samples, and blanks are analyzed under the same conditions; and
- The Contractor performs acceptably on the Performance Evaluation (PE) samples using this system.

9.1.2 Gas Chromatograph (GC)

9.1.2.1 The following are the recommended GC analytical conditions. These conditions are recommended unless otherwise noted.

Capillary Columns

Carrier Gas:	Helium
Flow Rate:	15 mL/min.
Initial Temperature:	10°C
Initial Hold Time:	1.0 - 5.0 (±0.1) min.
Ramp Rate:	6°C/min.
Final Temperature:	160°C
Final Hold Time:	Until 3 min. after all compounds listed in Exhibit C (Low/Medium Volatiles) elute (required).

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the

analysis of all standards, samples, blanks, and Matrix Spikes/Matrix Spike Duplicates (MS/MSDs).

9.1.2.3 If the gaseous compounds chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0% from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10°C.

9.1.3 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Ionization Mode:	EI
Scan Time:	To give at least 5 scans per peak, not to exceed 2 sec. per scan for capillary column.

9.2 GC/MS Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.1).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing 4-bromofluorobenzene (BFB).

9.2.2 Frequency of GC/MS Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The 12-hour time period for GC/MS performance check, calibration standards (initial or continuing calibration verification), blank, and sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a Closing Continuing Calibration Verification (CCV) can be used as an opening CCV for the next 12-hour period, then an additional BFB tune is not required and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Performance Check

9.2.3.1 The analysis of the instrument performance check solution may be performed as follows:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding sufficient amount of BFB solution (Section 7.2.2.1) to 5 mL of reagent water to result in a 10 µg/L concentration of BFB.

- By adding sufficient amount of BFB solution to a calibration standard to result in a 10 µg/L concentration of BFB.

9.2.4 Technical Acceptance Criteria for GC/MS Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must be run under identical MS instrument conditions.

9.2.4.2 The analysis of the instrument performance check solution must meet the ion abundance criteria given in Table 1.

9.2.5 Corrective Action for GC/MS Performance Check

9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source, clean the quadrupole rods, or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 BFB technical acceptance criteria must be met before any standards, samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks, and after the instrument performance check solution criteria have been met, each GC/MS system must be calibrated at five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target and Deuterated Monitoring Compounds (DMCs).

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated upon award of the contract whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.) or if the continuing calibration verification acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze another continuing calibration verification standard. A method blank is required.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Assemble a purge-and-trap device that meets the specifications in Section 6.6. Condition the device as described in Section 9.1.1.

9.3.3.2 Connect the purge-and-trap device to the GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.1.2.

9.3.3.3 Add sufficient amount of the internal standard solution (Section 7.2.2.3) to each of the five aqueous calibration standard solutions (Section 7.2.2.6.2) containing the DMCs for a concentration of 50.0 µg/L at the time of purge. Analyze each calibration standard according to Section 10.

9.3.3.4 Separate initial calibration and continuing calibration verification must be performed for water samples and low-level soil/sediment samples if different purge conditions are used (unheated purge vs. heated purge). Extracts of medium-level soil/sediment samples may be analyzed using the calibrations of water samples if the same purge conditions are used.

The laboratory may run different matrices in the same 12-hour time period under the same tune, as long as separate calibration verifications are performed for each matrix within that 12-hour period.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the Relative Response Factor (RRF) for each volatile target and DMC using Equation 1. The primary characteristic ions used for quantitation are listed in Table 2. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in the same table. Assign the target compounds and DMCs to an internal standard according to Table 3.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_X = Area of the characteristic ion [Extracted Ion Current Profile (EICP)] for the compound to be measured (see Table 2).

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (see Table 2).

C_{is} = Concentration of the internal standard.

C_X = Concentration of the compound to be measured.

9.3.4.2 Calculating the RRFs of the xylenes requires special attention. Report an RRF for m- and p-xylene and one for o-xylene. On capillary columns, the m- and p-xylene isomers coelute. Therefore, when calculating the RRF in the equation above, use the area response (A_X) and concentration (C_X) of the peak from o-xylene and A_X and C_X of the peak from m- and p-xylene isomers.

9.3.4.3 The Mean Relative Response Factor ($\overline{RRF}$) must be calculated for all compounds.

9.3.4.4 Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for each purgeable target and DMC over the initial calibration range using Equation 2 in conjunction with Equations 3 and 4.

EQ. 2 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} \times 100$$

Where,

SD_{RRF} = Standard Deviation of initial calibration Relative Response Factors (per compound) from EQ. 3.

$\overline{X}$ = Mean value of the initial calibration Relative Response Factors (per compound).

9.3.4.5 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3 Standard Deviation Calculation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{(n-1)}}$$

Where,

X_i = Each individual value used to calculate the mean.

$\overline{X}$ = The mean of n values.

n = Total number of values.

9.3.4.6 Equation 4 is the general formula for the mean of a set of values.

EQ. 4 Mean Value Calculation

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Where,

X_i = Value.

$\overline{X}$ = Mean value.

n = Number of values.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2.6, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the BFB technical acceptance criteria.

9.3.5.2 The RRF at each calibration concentration for each purgeable target and DMC that has a required minimum RRF value must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4.

9.3.5.3 The %RSD for each target or DMC listed in Table 4 must be less than or equal to that value listed.

9.3.5.4 Up to two compounds may fail the criteria listed in Sections 9.3.5.2 and 9.3.5.3 and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0%.

9.3.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the purge-and-trap device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria must be met before any samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Opening and Closing Continuing Calibration Verification (CCV)

Prior to the analysis of samples and required blanks and after BFB tune and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV containing all the purgeable target compounds, DMCs, and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. A closing CCV using the same standard conditions as for the opening CCV is required after all samples and blanks have been analyzed, and before the end of the 12-hour time period.

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The 12-hour time period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may be added to the CCV solution, in which case only one injection is necessary. If a closing CCV meets the technical acceptance criteria for an opening CCV (Section 9.4.5) and samples are analyzed within that subsequent 12-hour time period, then an additional BFB tune is not required and the 12-hour time period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a BFB tune, followed by an opening CCV is required and the next 12-hour time period begins with the BFB tune.

9.4.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required. Quantitate all sample and blank results using the mean RRF obtained from the initial calibration standard.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 Set up the purge-and-trap GC/MS system per the requirements in Section 9.1.1.

9.4.3.2 Add a sufficient amount of the internal standard solution (Section 7.2.2.3) to the 5 mL syringe or volumetric flask containing the continuing calibration verification (Section 7.2.2.6.4) to result in a concentration of 50 µg/L. Analyze the continuing calibration verification standard according to Section 10.

9.4.3.3 All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.4.3.4 For low-level soil samples, the continuing calibration verification standard shall be prepared in the same manner as the initial calibration standard of the same concentration as specified in Section 9.3.3.3.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each target compound and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the Percent Difference (%Difference) between the continuing calibration verification RRF_c and the most recent initial calibration $\overline{RRF_i}$ for each purgeable target compound and DMC using Equation 5.

EQ. 5 Percent Difference Calculation

$$\%Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

RRF_c = Relative Response Factor from current continuing calibration verification standard.

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration.

9.4.5 Technical Acceptance Criteria for Opening and Closing CCV

9.4.5.1 The concentration of the low/medium volatile organic target and DMCs in the opening and closing CCV must be at or near the midpoint concentration level of the calibration standards, 5.0 µg/L for non-ketones, 10 µg/L for ketones, and 250 µg/L for 1,4-dioxane. The opening and closing CCV standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the BFB (Section 9.2.4) and initial calibration (Section 9.3.5) technical acceptance criteria.

9.4.5.2 For an opening CCV, the RRF for each purgeable target and DMC that has a required minimum RRF value must be greater than, or equal to, the compound's minimum acceptable RRF listed in Table 4. For a closing CCV, the RRF for each purgeable target and DMC must be at least 0.010.

9.4.5.3 For an opening CCV, the RRF Percent Difference for each purgeable target compound and DMC listed in Table 2 must be less than, or equal to, the value listed. For a closing CCV, the RRF Percent Difference for each purgeable target and DMC must be in the inclusive range of 50.

9.4.5.4 For an opening CCV, up to two compounds may fail the requirements listed in Sections 9.4.5.2 and 9.4.5.3 for an opening CCV and still meet the minimum RRF criteria and Percent Difference criteria. However, these compounds must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%. For a closing CCV, all compounds must meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3 for a closing CCV.

9.4.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument

operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Opening and Closing Continuing Calibration Verification (CCV)

9.4.6.1 If the opening CCV technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria are not met, then all samples and blanks analyzed within that 12-hour time period must be reanalyzed at no additional cost to USEPA. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.2 Continuing calibration verification technical acceptance criteria **MUST** be met before any samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when continuing calibration verification technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90%, of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to notify them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multi-phase samples (e.g., two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases, if required;
- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water Samples

10.1.3.1 Prior to the analysis of samples, establish the appropriate purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) operating conditions, as outlined in Section 9.1. Samples shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, and continuing calibration verification requirements. Also prior to sample analysis, a method blank must be analyzed that meets blank technical acceptance criteria in Section 12.1.4. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis. All samples, required blanks, and calibration standards must be analyzed under the same instrument conditions.

10.1.3.2 If time remains in the 12-hour period (as described in Section 9.3.2), samples may be analyzed without analysis of a continuing calibration verification standard.

10.1.3.3 Adjust the purge gas (helium) flow rate to 25-40 mL/minute. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

10.1.3.4 If the autosampler can automatically sample the appropriate volume then Sections 10.1.3.5 to 10.1.3.7 are performed by the autosampler.

10.1.3.5 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle that has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. This process of taking an aliquot destroys the validity of the sample for future analysis so, if there is only one VOA vial, the analyst must fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly. Filling one 5 mL syringe would allow the use of only one syringe. If an analysis is needed from the second 5 mL syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

10.1.3.6 Add a sufficient amount of Deuterated Monitoring Compound (DMC) spiking solution (Section 7.2.2.4) and a sufficient amount of internal standard spiking solution (Section 7.2.2.3) through the valve bore of the syringe, then close the valve. The DMCs and internal standards may be mixed and added as a single spiking solution.

NOTE: Purge-and-trap instrumentation that allows internal standard and DMCs to be automatically added to each sample is widely available.

Some of this instrumentation may be set-up by the manufacturer to add only 1 µL of internal standard or DMCs. The 1 µL addition of standards will be allowed if the addition is done solely in an automated manner, and if the final concentration of the standard in the 5 mL water sample remains 50 µg/L.

10.1.3.7 Attach the valve assembly on the syringe to the valve on the sample purger. Open the valves and inject the sample into the purging chamber.

10.1.3.8 Close both valves and purge the sample for 11.0 (±0.1) minutes at ambient temperature.

10.1.3.9 Sample Desorption - After the 11-minute purge, attach the trap to the GC, adjust the purge-and-trap system to desorb mode, initiate the temperature program sequence of the GC, and start data acquisition. Introduce the trapped material into the GC column by rapidly heating the trap to 180°C while backflushing the trap with inert gas at 15 mL/min. for 4.0 ±0.1 minutes. While the trapped material is being introduced into the GC, empty the sample purger and rinse it with reagent water. For samples containing large

amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the sample purger with a detergent solution, rinse it with reagent water, and then dry it in an oven at 105°C.

10.1.3.10 Trap Reconditioning - After desorbing the sample, recondition the trap for a minimum of 7.0 (±0.1) minutes at 180°C by returning the purge-and-trap system to purge mode. Trap temperatures up to 220°C may be employed. However, higher temperatures will shorten the useful life of the trap.

10.1.3.11 Gas Chromatography - Hold the column temperature at 10°C for 1.0 - 5.0 min., then program at 6°C/min. to 160°C and hold until 3 minutes after all target volatile compounds have eluted.

NOTE: Once an initial hold time has been chosen and the GC operating conditions optimized, the same GC condition must be used for the analysis.

10.1.3.12 Termination of Data Acquisition - 3 minutes after all the purgeable target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate Extracted Ion Current Profiles (EICPs).

10.1.4 Low-Level Soil/Sediment Samples

10.1.4.1 The Contractor should strive to analyze soil/sediment samples at the lowest dilution, unless directed otherwise. If samples are received as sealed VOA vials or containers, they are to be analyzed according to Section 10.1.4.2 (Method 5035), unless screening analysis indicates samples are to be analyzed as medium-level samples. If the results of medium-level analysis indicate that all target compound concentrations are below the medium-level Contract Required Quantitation Limit (CRQL) in Exhibit C (Low/Medium Volatiles), then the samples must be analyzed as low-level samples. If samples are originally analyzed by the low-level method, and any target compound on-column amount in a sample is greater than 3000 ng (6000 ng for ketones, 75,000 ng for 1,4-dioxane), then the sample is to be reanalyzed by the medium-level method. In this scenario, the low-level analysis, the medium-level analysis, and any dilution of the medium-level samples are billable.

If USEPA specifically requests the laboratory to analyze a sample only by the medium-level protocol (i.e., methanol extraction technique), the laboratory is not obligated to perform the low-level analysis. The request to the laboratory is to be made on the Traffic Report/Chain of Custody (TR/COC) Record. After receiving a TR/COC Record with this specific request, the laboratory is to confirm the request through SMO.

10.1.4.2 The following steps apply to the preparation of vials used for the analysis of low-level soil/sediment samples by the closed-system purge-and-trap equipment described in this method.

NOTE: There should be three field core sampling/storage containers for each field sample. The contents of two of the field core containers are to be processed using the steps outlined in Sections 10.1.4.3 - 10.1.4.8. One of these prepared samples is then to be used as the primary sample, while the

other is to be used as a back-up sample, if necessary. The contents of the third field core container shall be transferred to a tared dry closed-system purge-and-trap container (i.e., no preservative solution or stirring bar is to be added), weighed according to Section 10.1.4.8, and then stored at less than -7°C. This sample shall be used for the medium concentration level methanol extraction procedure as described in Section 10.1.4.1, if results of the original analysis indicate that medium-level extraction is warranted.

10.1.4.3 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

10.1.4.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted vials are used, seal both ends as recommended by the manufacturer.

10.1.4.5 Affix a label to each vial and weigh the prepared vial to the nearest 0.01 g. Record the tare weight and final weight.

10.1.4.6 Because volatile organics will partition into the headspace of the vial and will be lost when the vial is opened, DMCs, Matrix Spikes, and internal standards should only be added to vials after the sample has been added to the vial. The standards should be introduced either manually by puncturing the septum with a small-gauge needle or automatically by the purge-and-trap system just prior to analysis.

10.1.4.7 Using the sample collection device, transfer the contents (approximately 5 g) into the sample vial. This sample transfer must be performed rapidly to minimize loss of volatile compounds. Quickly brush any soil off the vial and immediately seal the vial with the septum and screw-cap. The soil vial is hermetically sealed and must remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. Record the date and time of sample transfer onto the pre-prepared vials and submit with the data package.

10.1.4.8 Weigh the vial and contents to the nearest 0.01 g and record this weight. Sample weight is determined by subtracting the sample vial tared weight determined above from this final weight.

10.1.4.9 Prior to sample purge, all soil/sediment samples must be allowed to warm to ambient temperature. For those samples that have been stored in freezing compartments and will be analyzed by the low concentration level protocol, 5 mL of reagent water must be added to the vials without disturbing the hermetic seal of the sample vial.

NOTE: An additional 5 mL of reagent water will be added to the vial as per Section 10.1.4.10.

Shake all vials containing aqueous solutions gently to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

10.1.4.10 Without disturbing the hermetic seal on the sample vial, add 5 mL reagent water, add sufficient amount of the internal standard spiking solution (Section 7.2.2.3) and the DMC spiking solution (Section 7.2.2.4). All samples, including MS/MSDs, standards, and blanks, within an SDG, must have the same amount of reagent water added. Do not increase/change the amount of DMC and internal standard solution added. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

10.1.4.11 Purge the sample with helium or another inert gas at a flow rate of 20 to 40 mL/minute for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

10.1.4.12 If a non-cryogenic interface is to be utilized, place the purge-and-trap system in the desorb mode after the 11-minute purge, and preheat the trap to 180°C without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about 4 minutes. Begin the temperature program of the GC and start data acquisition.

10.1.4.13 If a cryogenic interface is to be utilized, place the purge-and-trap system in the desorb mode after the 11-minute purge, making sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes. At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the GC and start the data acquisition.

10.1.4.14 After desorbing the sample for 4-5 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 180°C. After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool (ambient temperature), the next sample can be analyzed.

10.1.5 Medium-Level Soil/Sediment Samples

10.1.5.1 The medium-level soil/sediment method is based on extracting the soil/sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the DMCs and the internal standards. The reagent water containing the methanol extract is purged at ambient temperature.

10.1.5.2 Prior to the analysis of samples, establish the appropriate purge-and-trap GC/MS operating conditions, as outlined in Section 9.1. Because the methanol extract and reagent water mixture is purged at ambient temperature, the instrument performance check, initial calibration, and continuing calibration verification for water samples may be used for analyses of medium-level soil/sediment sample extracts.

10.1.5.3 The sample (for volatile organics) is defined as the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 5 g (wet weight) into a tared 15 mL vial. Use a top loading balance. Record the actual weight to the nearest 0.1 g.

NOTE: If a methanol preserved sample is to be analyzed, weigh the sample vial and contents to the nearest 0.1 g and record the weight. Record any discrepancies between laboratory-determined weight and sampler-determined weight in the SDG Narrative and utilize the sampler-determined weight in any calculations. Proceed to Section 10.1.5.6.

10.1.5.4 Quickly add 10 mL of methanol to the vial. Cap and shake for 2 minutes.

NOTE: The steps in Sections 10.1.5.3 and 10.1.5.4 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

10.1.5.5 Let the solution settle. Then, using a disposable pipette, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be discarded. The 1 mL extract may be stored in the dark at 4°C (±2°C) prior to the analysis.

10.1.5.6 Add 100 µL volume of methanol extract to the 5 mL of reagent water for analysis. Otherwise, estimate the concentration range of the sample from the low-level analysis or from the in-house screening procedure to determine the appropriate volume. A 100 µL of methanol extract is the maximum volume that can be added to the 5 mL of reagent water for medium-level analysis.

10.1.5.7 Remove the plunger from a 5 mL Luer-Lok type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards. Add 20 µL of DMC spiking solution (Section 7.2.2.4) and sufficient amount of internal standard spiking solution (Section 7.2.2.3). Also add the volume of methanol extract determined in Section 10.1.5.6 and a volume of clean methanol to total 100 µL (excluding methanol in DMC/internal standard solutions).

10.1.5.8 Attach the syringe-syringe valve assembly to the syringe valve on the purge device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

10.1.5.9 Proceed with the analysis as outlined in Sections 10.1.3.8 - 10.1.3.12.

10.1.6 Sample Dilutions

10.1.6.1 The Contractor shall analyze samples undiluted, or at minimal dilution. Samples may be diluted because of target compound responses exceeding the response of the same target compound in the high standard, or because of excessive matrix interference that hinders accurate quantitation. It is highly recommended that screening analysis be performed prior to sample analysis to determine estimated compound concentration and matrix problems.

NOTE 1: If the laboratory has evidence or highly suspects, because of sample color or other physical properties, that a sample may contain high concentrations of either target or non-target compounds, then SMO shall be contacted immediately. SMO will seek Regional recommendations for diluted analysis.

NOTE 2: Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate a Relative Response Factor (RRF) using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative.

10.1.6.2 For water samples, samples may be diluted to keep target compound concentrations within the calibrated range and/or to keep baseline height from the earliest eluting peak from exceeding one-half the relative height of the highest peak in the chromatogram. If dilution is required due to baseline drift, the laboratory must submit chromatograms in which the highest peak is set to full scale. If the baseline rises less than 10% in the diluted analysis, the sample has been overdiluted. The Contractor must receive prior approval from the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) of sample origin to perform more than two dilutions of a sample.

10.1.6.3 For soil samples, if the response of any target compound in the sample exceeds the response of the same target compound in the high standard, but the on-column amount of the target compound in the sample is less than 3000 ng, a new sample must be prepared according to Section 10.1.4.2 using the appropriate sample weight (i.e., less than 5.0 g). The sample weight should be chosen so that the target compound is in the top half of the calibration range. A minimum sample weight of 1.0 g must be used. If a sample weight of less than 1.0 g is required for the target compounds to be within the calibration range, then the Region should be contacted for further instructions.

10.1.6.4 The Dilution Factor (DF) chosen should keep the responses of the volatile target compounds that required dilutions in the upper half of the initial calibration range.

10.1.6.5 All dilutions must be made just prior to GC/MS analysis of the sample. Until the diluted sample is in a gas-tight syringe, all steps in the dilution procedure must be performed without delay.

10.1.6.6 For water samples, all dilutions are made in volumetric flasks. Select the volumetric flask that will allow for the necessary dilution (10-100 mL). Intermediate dilutions may be necessary for extremely large dilutions. Calculate the approximate volume of reagent water that will be added to the selected volumetric flask and add slightly less than this quantity of reagent water to the flask.

10.1.6.7 For water samples, inject the proper aliquot from the syringe prepared in Section 10.1.3.5 into the volumetric flask. Only aliquots of 1 mL increments are permitted. Dilute the aliquot to the mark on the flask with reagent water. Cap the flask, invert, and shake three times.

10.1.6.8 Fill a 5 mL syringe with the diluted sample as in Section 10.1.3.5. If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilutions.

10.1.6.9 Do **not** submit data for more than two analyses (i.e., from the original sample and **one** dilution) unless more than one dilution was required in order to bring all target compounds within

calibration range. Before performing a second dilution SMO should be contacted for further instructions. If the volatile screening procedure was employed, submit data from the most concentrated dilution analyzed and one further dilution.

10.2 pH Determination (Water Samples)

Once the sample aliquots have been taken from the VOA vial, the pH of the water sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the vial). Record the pH of each sample, and report these data in the SDG Narrative, following the instructions in Exhibit B. No pH adjustment is to be performed by the Contractor.

10.3 Percent Moisture Determination

It is highly recommended that the Percent Moisture (%Moisture) determination only be made after the analyst has determined that no sample aliquots will be taken from the 60 mL vial for further analysis. This is to minimize the loss of volatiles and to avoid sample contamination from the laboratory atmosphere.

Immediately after weighing the sample for analysis, weigh 5-10 g of the soil/sediment into a tared crucible. Determine the Percent Moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

EQ. 6 Percent Moisture Calculation

$$\%\text{Moisture} = \frac{\text{grams of wet sample - grams of dry sample}}{\text{grams of wet sample}} \times 100$$

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C (Low/Medium Volatiles) shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the same Gas Chromatograph (GC) Relative Retention Time (RRT) as the standard component; and
- Correspondence of the sample component and standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, use the RRT values from the 50 µg/L standard. Otherwise, use the corresponding opening CCV standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned by using Extracted Ion Current Profiles (EICP) or ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/Mass Spectrometer (MS) are required. Once obtained, these standard spectra may be used for identification purposes, **only** if the Contractor's GC/MS meets the daily instrument performance requirements for 4-bromofluorobenzene (BFB). These standard spectra may be obtained from the run used to obtain reference RRTs.

11.1.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) **must** be present in the sample spectrum.
- The relative intensities of ions specified in the above paragraph must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70%).
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the Contract Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "3J").

11.1.1.5 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.1.2 Qualitative Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later) or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as volatile target analytes using the procedures detailed in Section 11.1, or that are not DMCs or internal standards shall be tentatively identified via a forward search of the NIST or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane tentatively identified compounds of greatest apparent concentration shall be reported on Form I VOA-TIC. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes" on Form I VOA-TIC. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as tentative identified compounds on Form I VOA-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be qualified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Rules for making tentative identification:

11.1.2.4.1 For compounds to be reported, as per the instructions in Section 11.1.2.3., identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is <u>just evidence</u> not to report the compound as identified by the library search program.

11.1.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is <u>just</u> <u>evidence</u> not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the volatile target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is

identified as a DMC, internal standard, or volatile target analyte.

11.1.2.4.3 If the library search produces a series of obvious isomer compounds with library search matches greater that 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a tentatively identified compound has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialists is encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Identified target compounds shall be quantified by the internal standard method using Equation 7 or 8. The internal standard used shall be that which is assigned in Table 3. The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample.

11.2.1.2 Water

EQ. 7 Water Concentration Calculation

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\ (I_s)\ (DF)}{(A_{is})\ (\overline{RRF})\ (V_o)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target compounds, internal standards, and DMCs are listed in Table 2.

A_{is} = Area of the characteristic ion (EICP) for the internal standard. The target compounds are listed with their associated internal standards in Table 3.

I_s = Amount of internal standard added, in ng.

$\overline{RRF}$ = Mean Relative Response Factor from the initial calibration.

V_o = Total volume of water purged, in mL.

DF = Dilution Factor. The DF for analysis of water samples for volatiles by this method is defined as the ratio of the number of mL of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 2.0 mL of sample is diluted to 5.0 mL with reagent water and purged, DF = 5.0 mL/2.0 mL = 2.5. If no dilution is performed, DF = 1.0.

11.2.1.3 Low-Level Soil/Sediment

EQ. 8 Low-Level Soil/Sediment Concentration Calculation

$$\text{Concentration (µg/Kg) (dry weight basis)} = \frac{(A_x)\,(I_s)\,(DF)}{(A_{is})\,(\overline{RRF})\,(W_s)\,(D)}$$

Where,

A_x, I_s, A_{is}, and DF are as given for water, Equation 7.

$\overline{RRF}$ = Mean Relative Response Factor from the heated purge of the initial calibration.

$$D = \frac{100 - \%\text{Moisture}}{100}$$

W_s = Weight of sample added to the purge tube, in g.

11.2.1.4 Medium-Level Soil/Sediment

EQ. 9 Medium-Level Soil/Sediment Concentration Calculation

$$\text{Concentration µg/Kg (dry weight basis)} = \frac{(A_x)\,(I_s)\,(AV_t)\,(1000)\,(DF)}{(A_{is})\,(\overline{RRF})\,(V_a)\,(W_s)\,(D)}$$

Where,

A_x, I_s, A_{is} are as given for water, Equation 7.

$\overline{RRF}$ = Mean Relative Response Factor from the **ambient** temperature purge of the initial calibration.

AV_t = Adjusted total volume of the methanol extract plus soil water in milliliters (mL) determined by:

$AV_t = V_t + W_s - [W_s(D)]$

Where V_t = total volume of methanol extract in milliliters (mL). This volume is typically 10 mL, even though only 1.0 mL is transferred to the vial in Section 10.1.5.5.

V_a = Volume of the aliquot of the sample methanol extract (i.e., sample extract not including the methanol added to equal 100 µL), in microliters added to reagent water for purging.

W_s = Weight of soil/sediment extracted, in g.

$$D = \frac{100 - \%Moisture}{100}$$

DF = Dilution Factor. The DF for analysis of soil/sediment samples for volatiles by the medium-level method is defined as:

$$\frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

11.2.1.5 For water, low-level and medium-level soil/sediment samples, xylenes are to be reported as "m- and p-xylenes" and "o-xylene". Because m- and p-xylene isomers coelute, special attention must be given to the quantitation of the xylenes. In quantitating sample concentrations, be sure to use the correct corresponding RRF values.

NOTE: The area of each peak (i.e., the peaks for ortho-xylene and meta/para-xylene) must appear on the complete quantitation report.

11.2.1.6 The stereoisomers, trans-1,2-dichloroethene, and cis-1,2-dichloroethene are to be reported separately.

11.2.1.7 Secondary ion quantitation is allowed **only** when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the SDG Narrative. A secondary ion cannot be used unless an RRF is calculated using the secondary ion.

11.2.1.8 The requirements listed in Sections 11.2.1.9 and 11.2.1.10 apply to all standards, samples including Matrix Spikes/Matrix Spike Duplicates (MS/MSDs) and blanks.

11.2.1.9 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the

specific target compound, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.

11.2.1.10 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Low/Medium Volatiles), internal standards, and DMCs.

11.2.2 Non-Target Compounds

11.2.2.1 An estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 The formulas for calculating non-target compound concentrations are the same as in Sections 11.2.1.2, 11.2.1.3, and 11.2.1.4. Total area counts (or peak heights) from the total Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured (A_x) and the internal standard (A_{is}). An RRF of 1.0 is to be assumed. The value from this quantitation shall be qualified as "J" (estimated due to the lack of a compound-specific RRF), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all Tentatively Identified Compounds (TICs), as well as those identified as unknowns.

11.2.3 CRQL Calculations

11.2.3.1 Water

EQ. 10 Water Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{V_x}{V_o} \times DF$$

Where,

Contract CRQL = Exact CRQL values in Exhibit C of the Statement of Work (SOW).

V_o and DF are as given in Equation 7.

V_x = Contract Sample Volume (5.0 mL).

11.2.3.2 Low-Level Soil/Sediment

EQ. 11 Low-Level Soil Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_x)}{(W_s)(D)}$$

Where,

W_s and D are as given in Equation 8.

W_x = Contract Sample Weight (5.0 g).

11.2.3.3 Medium-Level Soil/Sediment

EQ. 12 Medium-Level Soil/Sediment Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_x)(V_t)(V_y)(1000)(DF)}{(W_s)(V_c)(V_a)(D)}$$

Where,

V_t, DF, W_s, V_a and D are as given in Equation 9.

W_x = Contract Sample Weight (5.0 g).

V_y = Contract Soil Aliquot Volume from soil methanol extract (100 µL).

V_c = Contract Soil Methanol Extract Volume (10,000 µL).

11.2.4 Deuterated Monitoring Compound (DMC) Recoveries

11.2.4.1 Calculate the concentration of each DMC using the same equation as used for target compounds.

11.2.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 13. Report the recoveries on the appropriate forms.

EQ. 13 DMC Percent Recovery Calculation

$$\%R = \frac{Q_d}{(Q_a \times DF)} \times 100$$

Where,

Q_d = Concentration or amount determined by analysis.

Q_a = Concentration or amount added to sample/blank.

DF = Same as EQ. 9.

11.2.5 Internal Standard Responses and Retention Times (RTs)

Internal standard responses and RTs in all samples must be evaluated during, or immediately after, data acquisition. Compare the sample/blank internal standard responses and RTs to the opening continuing calibration verification internal standard responses and RTs. For samples and blanks analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and RTs against the 50 µg/L calibration standard.

The EICP of the internal standards must be monitored and evaluated for each sample including Matrix Spikes and Matrix Spike Duplicates and blanks.

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The samples must be analyzed on a GC/MS system meeting the BFB, initial calibration, continuing calibration verification, and blank technical acceptance criteria.

11.3.2 The sample and any required dilution must be analyzed within the contract holding time.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The Percent Recovery of each of the DMCs in the sample must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory. Up to three DMCs, excluding 1,4-dioxane-d_8, per sample may fail to meet the recovery limits listed in Table 5.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of 50.0% and 200% of its response in the most recent opening continuing calibration verification standard analysis.

11.3.6 The RT shift for each of the internal standards in the sample must be within ±0.50 minutes (30 seconds) of its RT recent opening continuing calibration verification standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.1.6.

11.3.8 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (see Section 12.1.4); or

- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the calibration range. The maximum carryover criteria are as follows: the sample must not contain a

concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If an auto sampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum contamination criteria.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require reanalysis at no additional cost to USEPA.

11.4.2 Corrective actions for failure to meet instrument performance checks, initial calibration, continuing calibration verification, and method blanks must be completed before the analysis of samples.

11.4.3 Corrective Action for DMCs and Internal Standard Compounds that Fail to Meet Acceptance Criteria

11.4.3.1 If the technical acceptance criteria for any of the internal standards and DMCs are not met:

- Check all calculations, instrument logs, the DMC and internal standard compound spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the DMC recoveries and internal standard compound responses meet acceptance criteria.

- If the instrument logs indicate that the incorrect amount of DMC or internal standard compound spiking solution was added, then reanalyze the sample after adding the correct amount of DMC and internal standard spiking solutions.

- If the DMC spiking solution or internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solutions and reanalyze the samples.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument before re-analyzing the sample. Verify that the DMC recoveries meet acceptance criteria.

11.4.3.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If DMC recoveries or internal standard compound responses in a sample used for a Matrix Spike or Matrix Spike Duplicate (MS/MSD) were outside the acceptance criteria, then it should be reanalyzed only if DMC recoveries and internal standard compound responses met acceptance criteria in both the MS/MSD analyses.

- If the DMC recoveries and the internal standard compound responses meet the acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit data only from the reanalysis.

- If the DMC recoveries and/or the internal standard compound responses fail to meet the acceptance windows in the

reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B.

11.4.4 Corrective Action for Internal Standard Compound RTs Outside Acceptance Criteria

11.4.4.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument before re-analyzing the samples.

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If the internal standard compound RTs in a sample used for a MS or MSD were outside the acceptance criteria, then it should be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in both the MS/MSD analyses.

- If the internal standard compound RTs are within the acceptance criteria, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the internal standard compound RTs are within the acceptance limits.

- If the internal standard compound RTs are outside the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.5 All samples to be reported to USEPA must meet the maximum carryover criteria in Section 11.3.8. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross-contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks. If an instrument blank is not analyzed between consecutive samples that have the same compound with a concentration exceeding the calibration range then the second sample must be appropriately diluted as in Section 10.1.6.4 and analyzed. If in the dilution this compound is detected at levels at or below CRQL then all samples analyzed after the second sample that fail to meet maximum carryover criteria must be reanalyzed. If in the dilution this compound is detected within the calibration range then no further corrective action is required.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary

There are three different types of blanks required by this method.

12.1.1.1 Method Blank - A volume of a clean reference matrix (reagent water for water samples or a purified solid matrix for soil/sediment samples) spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and Deuterated Monitoring Compound (DMC) solution (Section 7.2.2.4), and carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

NOTE: For soil/sediment samples, if any samples are prepared without the sodium bisulphate preservative, a method blank will be prepared in the same manner and run in the same 12-hour sequence as the unpreserved samples.

12.1.1.2 Storage Blank - A volume of a clean reference matrix [reagent water for water samples stored at 4°C (±2°C) or inert sand for soil samples stored at less than -7°C] spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4), and analyzed after all samples in the Sample Delivery Group (SDG) have been analyzed. Upon receipt of the first samples in an SDG), two vials with a clean reference matrix are stored with the samples in the SDG under the same conditions. After all samples in the SDG have been analyzed, the storage blank is analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

NOTE: If the SDG contains samples stored at 4°C (±2°C) and samples stored at less than -7°C, two storage blanks will be prepared, one for each condition.

12.1.1.3 Instrument Blank - A 5.0 mL aliquot of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4) that is added to the sample vial and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target compound exceeding the initial calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The method blank **must** be analyzed at least once during every 12-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank **must** be analyzed after the opening continuing calibration verification and before any samples, including Matrix Spike/Matrix Spike Duplicates (MS/MSDs), dilutions, or storage blanks are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour period expires. A method blank must be analyzed in each

12-hour time period in which samples, including dilutions, MS/MSDs, and storage blanks from an SDG are analyzed.

12.1.2.3 A minimum of one storage blank must be analyzed per matrix type (1 for soil and 1 for water sample) after all samples for the SDG stored in the same manner have been analyzed, unless the SDG contains only ampulated Performance Evaluation (PE) samples. Analysis of a storage blank is not required for SDGs that contain only ampulated PE samples.

12.1.2.4 The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples may contain target compounds at levels exceeding the initial calibration range. An instrument blank must be analyzed after the sample that exceeds the calibration range (also in the same purge inlet if an autosampler is used) or a sample that meets the maximum contamination criteria in Section 11.3.8 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analyses or the sample meets the maximum contamination criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to USEPA.

NOTE: Only the instrument blank that demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.4.6) must be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.3.8 do not need to be reported.

12.1.3 Procedure for Blank Analyses

12.1.3.1 For water samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.1.3.

12.1.3.2 For low-level soil samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.1.4.

12.1.3.3 For medium-level soil samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.1.5.

12.1.3.4 Storage/instrument blanks shall be analyzed in the same manner as the associated samples following the procedures outlined in Section 10.1.

12.1.3.5 Under no circumstances should blanks (storage/instrument/method) be analyzed at a dilution (i.e., blanks should always have a DF = 1.0).

12.1.3.6 Identify and quantitate analytes according to Section 11.0.

12.1.4 Technical Acceptance Criteria for Blank Analyses

12.1.4.1 All blanks must be analyzed on a GC/MS system meeting the 4-bromofluorobenzene (BFB), initial calibration, and continuing calibration verification technical acceptance criteria and at the frequency described in Section 12.1.2.

12.1.4.2 The storage blank must be analyzed on a GC/MS system that also meets the technical acceptance criteria for the method blank.

12.1.4.3 The Percent Recovery (%R) of each of the DMCs in a blank must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory.

12.1.4.4 The Extracted Ion Current Profile (EICP) area for each of the internal standards in a blank must be within the range of 50.0% and 200% of the response of the internal standards in the most recent opening continuing calibration verification standard analysis.

12.1.4.5 The Retention Time (RT) shift for each of the internal standards in a blank must be within ±0.50 min. (30 sec.) of its RT in the most recent opening continuing calibration verification standard analysis.

12.1.4.6 The concentration of each target compound found in the blank must be less than the Contract Required Quantitation Limit (CRQL) listed in Exhibit C (Low/Medium Volatiles), except for methylene chloride, acetone, and 2-butanone which must be less than 2 times the respective CRQL. The concentration of each target compound in the instrument blank must be less than its CRQL listed in Exhibit C (Low/Medium Volatiles).

12.1.5 Corrective Action for Blank Analyses

12.1.5.1 It is the Contractor's responsibility to ensure that method interferences caused by the contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in Gas Chromatograms, be eliminated. If a Contractor's blanks exceed the criteria in Section 12.1.4.6, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures **MUST** be taken and documented before further analysis proceeds.

12.1.5.2 Any method blank that fails to meet the technical acceptance criteria must be reanalyzed. Further, all samples processed within the 12-hour time period with a method blank that does not meet the blank technical acceptance criteria will require reanalysis at no additional cost to USEPA.

Any instrument blank that fails to meet any technical acceptance criteria described in Sections 12.1.4.3 through 12.1.4.6 requires reanalysis of the samples analyzed after the instrument blank having any target compounds detected at levels above CRQL.

12.1.5.3 If the storage blank does not meet the technical acceptance criteria for blank analyses in Sections 12.1.4.1 - 12.1.4.5, correct system problems and reanalyze the storage blank. If the storage blank does not meet the criteria in Section 12.1.4.6, reanalyze the storage blank to determine whether the contamination occurred during storage or during analyses. If, upon reanalysis, the storage blank meets the criteria in Section 12.1.4.6, the

problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank did not meet the criteria in Section 12.1.4.6, the problem occurred during storage. The Laboratory Manager or their designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

NOTE: A copy of the storage blank data must also be retained by the Contractor and be made available for inspection during on-site laboratory evaluations.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for volatile analyses, USEPA has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD

12.2.2.1 An MS/MSD shall be analyzed if requested by the Region [through the Sample Management Office (SMO)] or specified on the Traffic Report/Chain of Custody (TR/COC) Record. If requested, a Matrix Spike and a Matrix Spike Duplicate must be performed for each group of 20 field samples in an SDG, or each SDG, whichever is most frequent.

12.2.2.2 As a part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 If the USEPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample, less than the required amount to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of a sample other than the one designated by the Region shall be documented in the SDG Narrative.

12.2.2.4 If an insufficient number of sample vials were received to perform an MS/MSD, and MS/MSD are required, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or specify an alternate means of performing the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than required by the contract, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD analysis performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid

for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives **only** PE sample(s), no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD when the Region did not designate samples to be used for this purpose. SMO will notify the Contractor of the chosen sample. The Contractor shall document the decision in the SDG Narrative.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 To prepare an MS/MSD for water samples, add 20 µL of the Matrix Spiking solution (Section 7.2.2.5) to each of the 5 mL aliquots of the sample chosen for spiking. Process samples according to Sections 10.1.3.5 - 10.1.3.12. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each Matrix Spike compound.

12.2.3.2 To prepare an MS/MSD for low-level soil/sediment samples, add 20 µL of the Matrix Spiking solution (Section 7.2.2.5) either manually by puncturing the septum with a small-gauge needle or automatically by the purge-and-trap system just prior to analysis. Analyze the MS/MSD samples by the procedure described in Section 10.1.4. Do not further dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

12.2.3.3 To prepare an MS/MSD for medium-level soil/sediment samples, add 8.0 mL of methanol and 2.0 mL of Matrix Spiking solution to each of the two aliquots of the soil/sediment sample chosen for spiking.

NOTE: In the cases where methanol has been added as a preservative, do not add additional methanol. Add only 2.0 mL of Matrix spiking solution to each of the two aliquots of the soil/sediment sample chosen for spiking.

Process samples according to Sections 10.1.5.6 - 10.1.5.9. This results in a 5,000 µg/kg concentration of each Matrix Spike compound when added to a 5 g sample. Add a 100 µL aliquot of this extract to 5 mL of water for purging (as per Sections 10.1.5.6 and 10.1.5.7).

NOTE: Before performing an MS/MSD analysis, analyze the sample used for MS/MSD. If the sample analysis requires dilution, the aliquots for the MS/MSD shall be prepared at the same dilution as the least diluted analysis for which the sample results will be reported to USEPA. Sample dilutions must be performed in accordance with Section 10.1.6. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the Matrix Spike compounds using the same equations as used for target compounds (Equations 7, 8, and 9). Calculate the recovery of each Matrix Spike compound as follows:

EQ. 14 Matrix Spike Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result.

SR = Sample Result.

SA = Spike Added.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 15 Relative Percent Difference Calculation

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

The vertical bars in the formula above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial calibration and continuing calibration verification technical acceptance criteria, blank technical acceptance criteria, and at the frequency described in Section 12.2.2.

12.2.5.2 The MS/MSD must be analyzed within the contract holding time.

12.2.5.3 The RT shift for each of the internal standards in the MS/MSD must be within ±0.50 minutes (30 seconds) of its RT and the most recent opening continuing calibration verification standard analysis.

12.2.5.4 The limits for Matrix Spike compound recovery and RPD are given in Table 6. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3, must be reanalyzed at no additional cost to USEPA.

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under the contract, the MDL for each volatile target compound shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water, low-level soil and medium-level soils). The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), GC column, and replacement or overhaul of the purge-and-trap device.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1) spiked with each volatile target compound at a concentration equal to 1-4 times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. MDL verification for low-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for low-level soil samples in Section 12.1) spiked with each volatile target compound at a concentration equal to two times the analytically determined MDL. MDL verification for medium-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for medium-level soil samples in Section 12.1) spiked with each volatile target compound at a concentration equal to two times the analytically determined MDL. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Section 11.1.1.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

US Environmental Protection Agency. Purge-and-Trap for Aqueous Samples. Method 5030C. Revision 2. May 2003.

US Environmental Protection Agency. Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples. Method 5035A. July 2002.

US Environmental Protection Agency. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Method 8260B. Revision 2. December 1996.

US Environmental Protection Agency. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. Method 524.2. August 1992.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

4-bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15.0-40.0% of mass 95
75	30.0-80.0% of mass 95
95	base peak, 100% Relative Abundance
96	5.0-9.0% of mass 95 (see NOTE)
173	less than 2.0% of mass 174
174	50.0-120% of mass 95
175	greater than 5.0-9.0% of mass 174
176	95.0-101% of mass 174
177	5.0-9.0% of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z

Table 2

Characteristic Ions for Volatile Target Compounds

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 63
1,1,2-Trichloro-1,2,2-trifluoroethane	101	85, 151
Acetone	43	58
Carbon disulfide	76	78
Methyl acetate	43	74
Methylene chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98
Methyl tert-butyl ether	73	43, 57
1,1-Dichloroethane	63	65, 83
cis-1,2-Dichloroethene	96	61, 98
2-Butanone	43[1]	72
Chloroform	83	85
Bromochloromethane	128	49, 51, 130
1,1,1-Trichloroethane	97	61, 99
Cyclohexane	56	69, 84
Carbon tetrachloride	117	119
Benzene	78	-
1,2-Dichloroethane	62	98
1,4-Dioxane	88	43,58
Trichloroethene	95	97, 130, 132
Methylcyclohexane	83	55, 98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127

[1]m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Table 2

Characteristic Ions for Volatile Target Compounds (Con't)

Deuterated Monitoring Compounds	Primary Quantitation Ion	Secondary Ion(s)
Vinyl chloride-d_3	65	67
Chloroethane-d_5	69	71, 51
1,1-Dichloroethene-d_2	63	98, 65
2-Butanone-d_5	46	77
Chloroform-d	84	86, 47, 49
1,2-Dichloroethane-d_4	65	67, 51
Benzene-d_6	84	82, 54, 52
1,2-Dichloropropane-d_6	67	65, 46, 42
Toluene-d_8	98	100, 42
trans-1,3-Dichloropropene-d_4	79	81, 42
2-Hexanone-d_5	63	46
1,4-Dioxane-d_8	96	51, 66
1,1,2,2-Tetrachloroethane-d_2	84	86
1,2-Dichlorobenzene-d_4	152	150
Internal Standards	**Primary Quantitation Ion**	**Secondary Ion(s)**
1,4-Dichlorobenzene-d_4	152	115, 150
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

Table 3

Volatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation

1,4-Difluorobenzene (IS)	Chlorobenzene-d_5 (IS)	1,4-Dichlorobenzene-d_4 (IS)
Dichlorodifluoromethane	1,1,1-Trichloroethane	Bromoform
Chloromethane	Cyclohexane	1,3-Dichlorobenzene
Vinyl chloride	Carbon tetrachloride	1,4-Dichlorobenzene
Bromomethane	Benzene	1,2-Dichlorobenzene
Chloroethane	Trichloroethene	1,2-Dibromo-3-chloropropane
Trichlorofluoromethane	Methylcyclohexane	1,2,4-Trichlorobenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-Trichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2-Dichlorobenzene-d_4 (DMC)
Acetone	cis-1,3-Dichloropropene	
Carbon disulfide	4-Methyl-2-pentanone	
Methyl acetate	Toluene	
Bromochloromethane	trans-1,3-Dichloropropene	
Methylene chloride	1,1,2-Trichloroethane	
trans-1,2-Dichloroethene	Tetrachloroethene	
Methyl tert-butyl ether	2-Hexanone	
1,1-Dichloroethane	Dibromochloromethane	
cis-1,2-Dichloroethene	1,2-Dibromoethane	
2-Butanone	Chlorobenzene	
Chloroform	Ethylbenzene	
1,2-Dichloroethane	m- and p-Xylenes	
1,4-Dioxane	o-Xylene	
Vinyl chloride-d_3 (DMC)	Styrene	
Chloroethane-d_5 (DMC)	Isopropylbenzene	
1,1-Dichloroethene-d_2 (DMC)	1,1,2,2-Tetrachloroethane	
2-Butanone-d_5 (DMC)	Benzene-d_6 (DMC)	
Chloroform-d (DMC)	1,2-Dichloropropane-d_6 (DMC)	
1,2-Dichloroethane-d_4 (DMC)	trans-1,3-Dichloropropene-d_4 (DMC)	
1,4-Dioxane-d_8 (DMC)	Toluene-d_8 (DMC)	
	2-Hexanone-d_5 (DMC)	
	1,1,2,2-Tetrachloroethane-d_2 (DMC)	

Table 4

Relative Response Factor Criteria for Initial and Opening Continuing Calibration Verification of Volatile Organic Compounds

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Dichlorodifluoromethane	0.010	40.0	±40.0
Chloromethane	0.010	40.0	±40.0
Vinyl chloride	0.100	20.0	±25.0
Bromomethane	0.100	20.0	±25.0
Chloroethane	0.010	40.0	±40.0
Trichlorofluoromethane	0.010	40.0	±40.0
1,1-Dichloroethene	0.100	20.0	±25.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	40.0	±40.0
Acetone	0.010	40.0	±40.0
Carbon disulfide	0.010	40.0	±40.0
Methyl acetate	0.010	40.0	±40.0
Methylene chloride	0.010	40.0	±40.0
trans-1,2-Dichloroethene	0.010	40.0	±40.0
Methyl tert-butyl ether	0.010	40.0	±40.0
1,1-Dichloroethane	0.200	20.0	±25.0
cis-1,2-Dichloroethene	0.010	40.0	±40.0
2-Butanone	0.010	40.0	±40.0
Bromochloromethane	0.050	20.0	±25.0
Chloroform	0.200	20.0	±25.0
1,1,1-Trichloroethane	0.100	20.0	±25.0
Cyclohexane	0.010	40.0	±40.0
Carbon tetrachloride	0.100	20.0	±25.0
Benzene	0.400	20.0	±25.0
1,2-Dichloroethane	0.100	20.0	±25.0
1,4-Dioxane	0.010	50.0	±50.0
Trichloroethene	0.300	20.0	±25.0
Methylcyclohexane	0.010	40.0	±40.0
1,2-Dichloropropane	0.010	40.0	±40.0
Bromodichloromethane	0.200	20.0	±25.0
cis-1,3-Dichloropropene	0.200	20.0	±25.0
4-Methyl-2-pentanone	0.010	40.0	±40.0
Toluene	0.400	20.0	±25.0

Table 4

Relative Response Factor Criteria for Initial and Opening Continuing Calibration Verification of Volatile Organic Compounds (Con't)

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
trans-1,3-Dichloropropene	0.100	20.0	±25.0
1,1,2-Trichloroethane	0.100	20.0	±25.0
Tetrachloroethene	0.100	20.0	±25.0
2-Hexanone	0.010	40.0	±40.0
Dibromochloromethane	0.100	20.0	±25.0
1,2-Dibromoethane	0.010	40.0	±40.0
Chlorobenzene	0.500	20.0	±25.0
Ethylbenzene	0.100	20.0	±25.0
m- and p-Xylenes	0.300	20.0	±25.0
o-Xylene	0.300	20.0	±25.0
Styrene	0.300	20.0	±25.0
Bromoform	0.050	20.0	±25.0
Isopropylbenzene	0.010	40.0	±40.0
1,1,2,2-Tetrachloroethane	0.300	20.0	±25.0
1,3-Dichlorobenzene	0.600	20.0	±25.0
1,4-Dichlorobenzene	0.500	20.0	±25.0
1,2-Dichlorobenzene	0.400	20.0	±25.0
1,2-Dibromo-3-chloropropane	0.010	40.0	±40.0
1,2,4-Trichlorobenzene	0.200	20.0	±25.0
1,2,3-Trichlorobenzene	0.200	20.0	±25.0
Deuterated Monitoring Compounds			
Vinyl chloride-d_3	0.010	20.0	±25.0
Chloroethane-d_5	0.010	40.0	±40.0
1,1-Dichloroethene-d_2	0.010	20.0	±25.0
2-Butanone-d_5	0.010	40.0	±40.0
Chloroform-d	0.010	20.0	±25.0
1,2-Dichloroethane-d_4	0.010	20.0	±25.0
Benzene-d_6	0.010	20.0	±25.0
1,2-Dichloropropane-d_6	0.010	40.0	±40.0
Toluene-d_8	0.010	20.0	±25.0

Table 4

Relative Response Factor Criteria for Initial and Opening Continuing Calibration Verification of Volatile Organic Compounds (Con't)

Deuterated Monitoring Compounds	Minimum RRF	Maximum	Maximum %Diff[1]
trans-1,3-Dichloropropene-d_4	0.010	20.0	±25.0
2-Hexanone-d_5	0.010	40.0	±40.0
1,4-Dioxane-d_8	0.010	50.0	±50.0
1,1,2,2-Tetrachloroethane-d_2	0.010	20.0	±25.0
1,2-Dichlorobenzene-d_4	0.010	20.0	±25.0

[1]For closing CCV, all target compounds and DMCs must meet a minimum RRF of 0.010 and a maximum percent difference of ± 50.0.

Table 5

Deuterated Monitoring Compound Recovery Limits

Compound	Percent Recovery for Water Samples	Percent Recovery for Soil Samples
Vinyl chloride-d_3	65-131	(68-122)
Chloroethane-d_5	71-131	(61-130)
1,1-Dichloroethene-d_2	55-104	(45-132)
2-Butanone-d_5	49-155	(20-182)
Chloroform-d	78-121	(72-123)
1,2-Dichloroethane-d_4	78-129	(79-122)
Benzene-d_6	77-124	(80-121)
1,2-Dichloropropane-d_6	79-124	(74-124)
Toluene-d_8	77-121	(78-121)
trans-1,3-Dichloropropene-d_4	73-121	(72-130)
2-Hexanone-d_5	28-135	(17-184)
1,4-Dioxane-d_8	50-150	(50-150)
1,1,2,2-Tetrachloroethane-d_2	73-125	(56-161)
1,2-Dichlorobenzene-d_4	80-131	(70-131)

NOTE: The recovery limits for any of the compounds listed above may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

Table 6

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
1,1-Dichloroethene	61-145	0-14	59-172	0-22
Trichloroethene	71-120	0-14	62-137	0-24
Benzene	76-127	0-11	66-142	0-21
Toluene	76-125	0-13	59-139	0-21
Chlorobenzene	75-130	0-13	60-133	0-21